Gas-phase femtosecond transient absorption spectroscopy

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A setup for measuring femtosecond transient absorption in the gas phase is reported. The apparatus is based on a 1 kHz amplified Ti:sapphire laser system and measures gas-phase transient absorption using a shot-to-shot normalization scheme with background subtraction. We have used this setup to examine the wave packet dynamics of the I_2 B state in the vapor phase as a benchmark. The results are consistent with those reported by other groups using indirect transient absorption techniques. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2221545]

I. INTRODUCTION

Transient absorption spectroscopy (TAS) has proven to be one of the most versatile techniques for studying ultrafast processes in chemistry and biology.[1] In a typical ultrafast TAS experiment, a pump laser pulse initiates the dynamics of a system by generating a nonstationary state that evolves in time. A second delayed probe pulse then probes the dynamics by measuring the optical absorption due to an upward transition (or optical gain due to a downward transition) as a function of the pump-probe delay time. Although femtosecond TAS has been widely used in condensed-phase ultrafast studies, its application in the gas phase has not been fully recognized. On the other hand, many variants of femtosecond TAS have been developed over the years to measure transient absorption spectra *indirectly* in the gas phase and have played crucial roles in the development of femtosecond transition-state spectroscopy[2,3] (FTS) and femtochemistry.[4] The detection methods used in these indirect femtosecond TAS techniques include laser-induced fluorescence (LIF),[5–7] ionization with mass[8–16] or photoelectron kinetic-energy[17–21] analyses, four-wave mixing,[22,23] (FWM) and coherent anti-Stokes Raman scattering (CARS).[24,25] These techniques yield, in principle, information equivalent or similar to those given in the transient absorption spectra. However, in the femtosecond pump-probe LIF the final levels in the probing step need to be fluorescing. This requirement is not always satisfied for large molecules in which the higher electronically excited states are usually weakly or even not fluorescing. This problem is surmounted in the femtosecond pump-probe ionization spectroscopy in which one-photon or multiphoton absorption leading to ionization implements the probing. The advantages are its compatibility with mass and/or photoelectron kinetic-energy analyses. However, in the case of multiphoton ionization (MPI) the possible involvement of several upper electronic states may complicate the interpretation, and in the case of one-photon ionization the difficulty in producing high-photon-energy femtosecond pulses may limit the systems of interest to those of low ionization potentials. For femtosecond-FWM and femtosecond CARS the probing steps rely on third-order nonlinear processes and therefore the analyses of the transient spectra are somewhat involved.[22,26] On the other hand, the direct femtosecond TAS method reported here measures the linear optical absorption of the probing transition itself, which should lead to a more straightforward interpretation. It does not require high-energy photons and is applicable for nonfluorescing systems. Thus, direct femtosecond TAS can complement other more popular techniques in exploring ultrafast dynamics in the gas phase.

In liquid-phase femtosecond TAS the solute concentrations are usually high enough to compensate for the very short path lengths required to minimize group velocity dispersion (GVD). In vapor-phase femtosecond TAS the molecular density is much lower, and therefore a much longer path length must be employed. Glownia *et al.* reported the first examples of gas-phase ultrafast transient absorption experiment with a subpicosecond time resolution.[27–29] Since then, gas-phase femtosecond TAS had gone unnoticed, probably due to its seemingly poor sensitivity. Here, we report a setup for measuring transient absorption in the gas phase with ~100 fs time resolution and reasonable sensitivity. In our experiments the femtosecond pump and probe beams were collinearly overlapped in a ~20 cm gas cell in order to compensate for the low molecular density and attain detectable absorbance changes. The temporal resolution was not deteriorated by the long path length because the GVD effect in low-pressure gases is negligible. We have used this setup to examine the wave packet dynamics of the I_2 B state in the vapor phase as a benchmark. In 1989 Bowman *et al.* employed femtosecond pump-probe LIF spectroscopy,[5] an indirect variant of the transient absorption, and observed the I_2 B-state wave packet dynamics. Since then I_2 vibrational wave packet motion had been studied by many different ultrafast spectroscopic techniques, including femtosecond MPI,[10,30] zero electron kinetic energy (ZEKE),[30,31] degenerate four-wave mixing (DFWM),[23] and CARS.[24]

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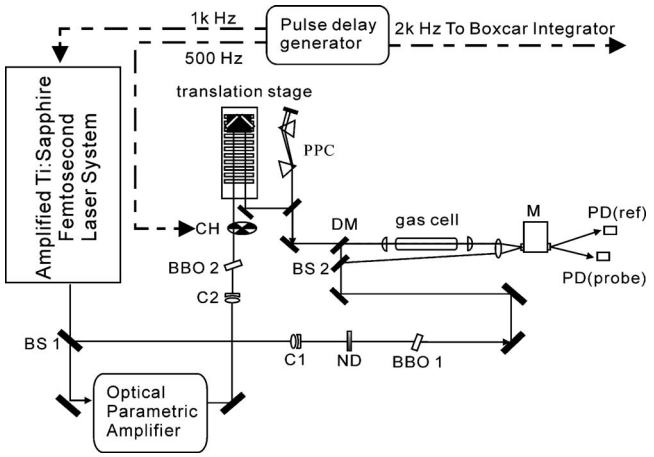

FIG. 1. Schematic diagram of the optical setup used in this experiment. CH=chopper, BBO=β-barium borate crystal, C=collimator, PPC=prism pair compressor, DM=dichroic mirror, ND=neutral density filter, PCL =planoconvex lens, M=monochromator, and PD=photodiode.

II. EXPERIMENTAL SETUP

A schematic diagram of our experimental setup is shown in Fig. 1. The laser pulses were derived from a femtosecond laser system consisting of a self-mode-locked Ti:sapphire laser (Spectra Physics, Tsunami), a 1 kHz chirped-pulse regenerative amplifier (CPA) (Spectra Physics, Spitfire) and a five-pass optical parametric generator/amplifier (Light Conversion, TOPAS). The CPA output was split into two parts by a beam splitter. The major part was used to pump the optical parametric amplifier whose signal output at ~1226 nm was frequency doubled by a thin β-barium borate (BBO) crystal to generate the pump pulse at ~613 nm. The pump beam was directed through a computer-controlled optical delay line and then sent through a prism-pair pulse compressor for GVD compensation.

The remaining part of the CPA output (800 nm) was frequency-doubled by another BBO crystal to obtain 400 nm femtosecond laser pulses that were subsequently divided by a beam splitter into the probe and reference beams with roughly equal intensities. The pump and probe beams were collinearly recombined by a dichroic mirror and focused through a f=200 mm lens into an ~20 cm long gas cell. The pump and probe pulse energies were about 10 and 1 μJ/pulse, respectively, before entering the cell, and the polarizations of the pump and probe beams were mutually perpendicular. After emerging from the cell, all three beams (pump, probe, and reference) were focused together onto the entrance slit of a small monochromator that served as a spectral filter to separate the pump and probe beams and to minimize the stray light. The probe and reference beams exiting the monochromator were then separately detected by two photodiodes. The output of each photodiode was fed into a boxcar integrator (Stanford Research, SR250) whose input was terminated by a 10 kΩ resistor. An optical chopper (Thorlabs, MC1000) was placed in the pump-beam path to modulate the excitation by blocking every other pump pulse. A third photodiode was used to monitor the modulation phase.

In order to remove the background offset fluctuation the boxcar integrators were triggered at twice the repetition rate of the CPA and operated in the active base line subtraction mode. A four-channel digital delay pulse generator (Berkeley Nucleonics Co., Model 555) was used as the master clock to synchronize the entire system. The fundamental output of the pulse generator at 2 kHz triggered the boxcar integrators, the divided-by-two output (1 kHz) triggered the CPA, while the divided-by-four output (500 Hz) was used to synchronize the optical chopper. The boxcar integrator offset was recorded between successive probe/reference pulses and was subtracted from the subsequent probe/reference pulse signal. This procedure effectively minimizes the offset fluctuation of the boxcar integrators. The outputs of the two integrators, including the probe, reference, and between-pulse-offset signal, were read by a 16 bits analog-digital converter (National Instrument, PCI-6036E) and then transferred to a computer for absorbance change calculations using a shot-to-shot normalization scheme. The sample cell was an ~20 cm long glass tube with 2 mm thick quartz windows on both ends. A few grains of iodine crystals were sealed in the sample cell at room temperature to give an iodine vapor pressure of ~100 mtorr.

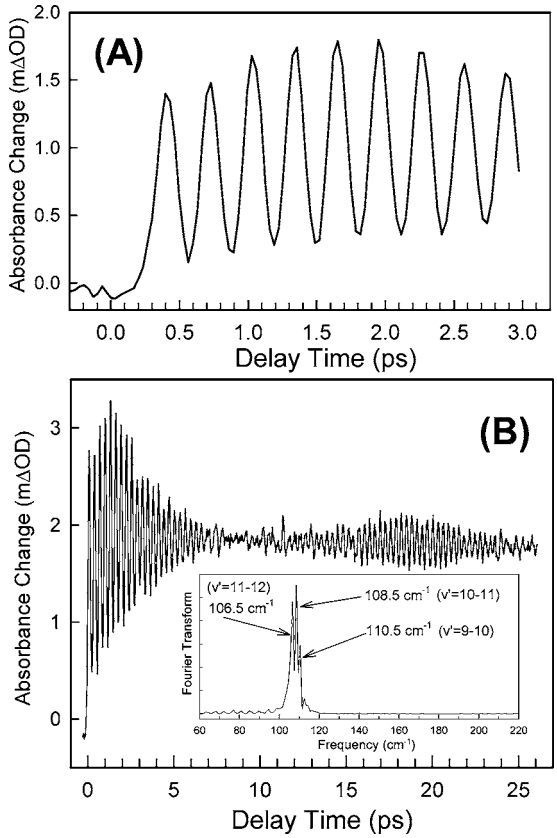

FIG. 2. Short-time scale (A) and long-time scale (B) gas-phase transient absorption traces of iodine vapor (~100 mtorr) excited at 613 nm and probed at 400 nm. The path length of the gas cell was about 20 cm, and the polarizations of the pump and probe beams were mutually orthogonal. The inset in (B) shows a Fourier transform power spectrum of the transient absorption trace. Three major frequency components were identified: 106.5, 108.5, and 110.5 cm^{-1}.

III. RESULTS AND DISCUSSION

Figure 2 shows the I_2 transient absorption transients ob-

tained using the setup described above. The transients are dominated by a rapid oscillation with a period of ~310 fs which are characteristic of vibrational wave packet motion of the I_2 B state.[32,33] The oscillation amplitude decreases with delay time and diminishes at about 8 ps and then reappears at about 14 ps. These dephasing and revival behaviors of vibrational wave packet have been well documented in the literature.[32,33] In the present case, the femtosecond pump pulse at 613 nm prepares a coherent superposition of several vibrational eigenstates, i.e., a vibrational wave packet. The different eigenstates evolve in time, causing the wave packet to move back and forth in the B-state potential well with an oscillation period determined by the average vibrational level spacing.[33] The probe pulse at 400 nm probes the wave packet motion by measuring the transient absorption of the evolving B-state wave packet to an upper electronic state, presumably the f_g state. The transient absorbance depends on the Franck-Condon overlap which is modulated by the wave packet motion in the B state, resulting in the observed rapid oscillation with a period of about 310 fs, as shown in Fig. 2(A). Excitation of iodine vapor at 613 nm accesses the B-state $v' \sim 10$ region (from $v''=2$) where the vibrational spacing is about 110 cm^{-1}, consistent with the observed 310 fs oscillation period. A Fourier transform (FT) power spectrum that reveals the frequency content of the transient is shown in Fig. 2(B) inset. Three major frequency components at 106.5, 108.5, and 110.5 cm^{-1} were identified. These are the results of a series of nearest neighbor coherence and the observed frequencies correspond to the vibrational level spacing of successive levels near $v'=10$. Because of anharmonicity a phase mismatch accumulates among the evolving vibrational eigenlevels and the wave packet gradually dephases. However, because the evolution of these eigenstates is coherent, they can rephase at later time and reproduce the wave packet. The revival time in Fig. 2(B) transient is about 20 ps, which is consistent with the reciprocal of the frequency difference of adjacent vibrational level spacing (~1.7 cm^{-1}) (Ref. 32) around $v'=10$. The lower oscillation amplitude in the revived oscillation is due to rotational dephasing.

The transients shown in Fig. 2 are in good agreement with those reported by Bowman *et al.* using femtosecond pump-probe LIF technique,[5] i.e., an indirect transient absorption method. However, the next-nearest-neighbor coherence, or the 2ω components were not observed in our experiment. This is due to the fact that our laser pulse width (~120 fs) was almost a factor of 2 longer than those used in Ref. 5, and therefore the coherent spectral width was not wide enough to bring about 2ω interference in our case. Fisher *et al.*[30] studied the same system using femtosecond pump-probe ionization spectroscopy with pulse widths comparable to ours, and indeed, the femtosecond pump-probe MPI transients reported in Ref. 30 are very similar to ours.

Although the transients shown in Fig. 2 were obtained with the pump and probe beams collinearly overlapped and focused, the signal did not only come from the small focal volume. In fact, when the focusing lens was removed and the two beams were collinearly overlapped along the beam path in the cell, similar transients with ΔOD of about an order of magnitude lower were obtained. This phenomenon is probably due to the inhomogeneous beam profiles that result in poor effective spatial overlap, and thus much lower ΔOD, when the laser beams are not focused. For the experiments described here a transient of S/N ~ 10 and a maximum ΔOD of 2×10^{-3} can be readily obtained at a scanning rate of 1000-laser-shots average per delay position. This corresponds to a lowest detectable ΔOD of about 2×10^{-4} at the same scanning rate. The high sensitivity and S/N ratio attained with the present setup promise its future applications to more complex molecular systems in the vapor phase. Note that the temporal resolution was not deteriorated by the long path length (~20 cm), suggesting that even longer path lengths can be used for less volatile compounds. Recently, we have successfully measured the vapor-phase transient absorption of o-hydroxy acetophenone (OHAP) excited at 320 nm and the preliminary results were consistent with what we observed previously using femtosecond pump-probe MPI detection.[11] In conclusion, although the realization of gas-phase femtosecond TAS is straightforward, the high sensitivity and temporal resolution demonstrated here suggest the applicability of femtosecond TAS to complement other more widely used techniques in exploring ultrafast dynamics in the gas phase. Upgrading the present setup to enable broadband detection using a white-light continuum probe is feasible and is now underway in our laboratory.

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